Development of UV-LED Phosphor Coatings for High Efficiency Solid State Lighting

Continuation Technical Report

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U. Happek

(706) 542-2859

(706) 542-2492 (FAX)

uhappek@physast.uga.edu

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The University of Georgia

Athens, Georgia 30602

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ABSTRACT

The University of Georgia, in collaboration with GE Global Research, is investigating the relevant quenching mechanism of phosphor coatings used in white light devices based on UV LEDs in a focused eighteen month program. The final goal is the design of high-efficacy white UV-LEDs through improved and optimized phosphor coatings. At the end of the first year, we have reached a fundamental understanding of quenching processes in UV-LED phosphors and have observed severe quenching in standard devices under extreme operating conditions. Relationships are being established that describe the performance of the phosphor as a function of photon flux, temperature, and phosphor composition. These relationships will provide a road map for the design of efficient white light LEDs during the final six months of the project.

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INTRODUCTION

The development of efficient solid state lighting (SSL) sources by 2020 will enable the reduction in annual lighting energy consumption for an annual savings of 0.74 quadrillion BTUs (quads). The acceptance of SSL sources will require complete flexibility in choosing the color temperature (CCT) and color rendering index (CRI) of the white light source. This can be achieved using a combination of UV-LEDs with phosphors that down-convert UV-LED radiation into visible light. The color of these lamps is completely controlled by the selection of appropriate phosphors, giving the required control over lamp color for many general illumination applications. However, achieving this goal will require the optimization of all aspects of the white LED lamp, including the phosphor efficiency.

In typical linear fluorescent lamps, the phosphor conversion (from Hg radiation) efficiency is $\geq 80\%$. However, in typical white LEDs, the phosphor conversion efficiency (from either blue or UV LED radiation) ranges from 40-60% depending upon the LED package and the phosphor selection. The goal of this program is to determine the fundamental causes of this lower phosphor conversion efficiency and to improve this efficiency by addressing these causes, either though phosphor or LED package design. The eventual goal for UV-LED phosphors is to match the conversion efficiency of typical fluorescent lamp coatings. Our effort can be summarized by the selection and evaluation of appropriate UV-LED phosphors, testing of these UV-LED phosphors in typical LED packages, identifying the phosphor quenching mechanisms within these packages, and fabricating improved LED lamps using the fundamental knowledge of quenching mechanisms.

Several major aspects of this program have been subcontracted from the University of Georgia. The identification and synthesis of optimized phosphors is subcontracted to GE Global Research using various GE proprietary phosphor compositions. In addition, the fabrication of all LED lamps has also been subcontracted to GE Global Research.

EXECUTIVE SUMMARY

The development of energy efficient solid state lighting based on phosphor coated UV-LEDs was outlined as a focused eighteen month project, because we found that the large fraction of the U.S. energy consumption for lighting (14 percent) necessitates the rapid development of energy efficient lighting that could replace the standard incandescent lamp. Within the first twelve months of the project the price for crude oil has almost doubled, and with it has risen the relevance of our project.

Among the different avenues for solid state lighting we have chosen the combination of UV-LED and phosphor coating, hereby duplicating the successful concept of gas-discharge based fluorescent lighting. Compared to standard fluorescent lighting phosphors, the conditions for UV-LED phosphors are extreme, due to the high photon flux and elevated temperatures in high power devices, and so-called quenching phenomena must be avoided in order to achieve energy efficient lighting.

To achieve this goal, the team included both material chemists from industry with an extensive background in phosphor materials and university based physicists specialized in solid state physics and luminescence.

In order to increase the efficacy of current devices, first an understanding of the fundamental processes in a phosphor material under conditions relevant to LED operation is needed. Task 1, the selection and synthesis of phosphors, and Task 2, the initial evaluation of the phosphors, were coupled in a feedback loop, i.e. often the experimental results stimulated the production of modified materials. Important in this context is the application of an experimental technique to identify ioinization processes in phosphor materials (see section on Experimental Techniques)

After the characterization of the bulk phosphor, prototype LED devices were fabricated (Task 3) and studied under standard (Task 3) and extreme (Task 4) conditions. While the first three tasks have been completed, Task 4 will continue for the remaining six months. Currently, we have established substantial quenching under extreme LED conditions, and we are in the process of determining whether this is due to the high photon flux in these devices and/or due to the elevated temperature in the phosphor layer. While we have adhered to the proposed road map through Task 3, we have deviated from our original proposal for temperature measurements within the phosphor layer in that we do not introduce dedicated probe ions into the phosphor layer, but use the temperature dependence of the phosphor decay and energy transfer rate. This not only simplifies our experiments, but also avoids possible ambiguities.

Task 5 consists of two parts: to establish design rules for UV-LED phosphor coatings and to design and fabricate improved devices based on these rules. We are currently in the process of finalizing the design rules.

The coming six months are crucial for the project, because we will be able to design an improved solid state lighting device based on the UV-LED parameters, i.e., the design rules will allow to optimize the coating for each LED design, and, in turn, we hope to advise the LED manufacturer on preferred LED geometries.

Within the present project, we have focused our attention on ionic phosphor materials. Most recently, broad band emitting covalent materials like sulfates and nitrides have been proposed for solid state lighting applications, and we hope to apply our approach to evaluate the potential of these novel materials.

EXPERIMENTAL TECHNIQUES

The arsenal of experimental techniques available include the entire range of optical characterization, including emission spectroscopy using CCD equipped spectrographs (five), photoexcitation, and photon-counting techniques to study relaxation phenomena. The photon counting equipment includes multichannel scalers with a time resolution of 5 nsec, higher temporal resolution can be achieved with time-to-Amplitude converters.
The excitation, emission and relaxation measurements are being performed at a large range of temperatures, necessary to establish temperature induced quenching phenomena. In addition to standard cryostats (eight) a "high temperature" cryostat was essential for our studies, allowing to vary the sample (phosphor) temperature between 10K and 500 K. Prototype LEDs were investigated by monitoring the emission spectrum and intensity as a function of input power. For investigations of transient phenomena, the LEDs were pulsed with a nsec pulse generator.
The original proposal included the utilization of ruby powder to measure the temperature distribution within the device. It turned out to be more practical, efficient, and less intrusive to use the temperature dependence the relaxation properties of the actual phosphor to monitor the phosphor layer temperature.
In terms of specialized techniques, we use Thermally Stimulated Luminescence Excitation Spectroscopy (TSLES) to identify photo-ionization processes in the phosphors. Photo-ionization is an important quenching mechanism, in addition, it can lead to long-term degradation of the phosphor material. This technique is exclusively used by our group, and has been developed with previous DOE funding.

TASK 1

Synthesis of Optimized LED Phosphors for Bulk Studies

This part of the project was carried out at the GE Corporate Research Center. Our GE collaborators took the lead in selecting promising UV-LED phosphors and also synthesized sufficient amounts of materials needed to complete the other tasks of this program. The materials provided included both simple and advanced phosphor blends. Important to note is the fabrication of D55/D65 blends for the UV-LED-Phosphor platform (see Task 2).

In order to achieve a fundamental understanding of the complex energy relaxation and energy transfer processes, single phosphor materials were provided as well. Moreover, in order to unravel the role of the activator concentration on the phosphor performance, concentration series were synthesized for a number of relevant materials.

This Task has been completed, and sufficient material is available for the continuation of the program.

TASK 2

Evaluation of Luminescence Properties of Bulk Phosphors

The optical evaluation of the bulk phosphors included photoexcitation, emission, and relaxation measurements for the single phosphors, and energy transfer studies for complex phosphor blends. In order to understand the complex absorption, emission and energy transfer processes in a phosphor blend, single phosphors were investigated in detail, including investigation of phosphors with different doping levels in order to distinguish single ion phenomena from collective ones. Important in Task 2 was the quantification of quenching parameters, i.e. the quenching temperature. In order to distinguish between level crossing and photoionization as the source of thermal quenching, thermally stimulated luminescence excitation spectroscopy was performed at UGA, a technique that was developed under previous DOE sponsorship.

This Task has been completed, D55/D65 spectra have been demonstrated and quenching mechanisms have been quantified.

TASK 3

Fabrication and Initial Evaluation of Prototype LED Devices

Prototype LED devices were fabricated at the GE Corporate Research Center and evaluated both at GE and UGA. Important aspects of this task were the monitoring of the emission spectrum in the LED package and the use of the LED chip to perform time-resolved measurements on the phosphor materials via pulsed operation of the LED. This Task has been completed, the required devices for the important Task 4 have been fabricated and characterized.

TASK 4

Evaluation of Phosphor Coatings in the LED package

Prototype LED devices are being investigated under standard and extreme conditions. Extreme conditions are an important aspect of this research, due to the rapid development of LED chips with increasing flux density. This task is ongoing and will continue through Q6, but we have reached an important milestone in our program that was defined as a go/no go decision point: the observation of strong non-linearities in the lumens vs. power curve. We are now in the process of identifying the origin of the quenching, with emphasis of the role of temperature and photon flux. Using temperature dependent phosphor properties (relaxation time, energy transfer rate) we are able to evaluate the temperature in situ, which will then allow us to design improved packaging for high efficient phosphor coatings for UV-LEDs.

This project is ongoing, a critical milestone has been reached (observation of quenching), the role of photon flux and temperature are being investigated.

TASK 5

Development of Optimized LED packages for Higher Efficacy LEDs

We have started with the development of design rules, primarily focused upon new packages using high power, high brightness UV-LEDs. After spectroscopic characterization (emission spectra, decay time, rise time, thermoluminescence) of the GE proprietary phosphors during LED operation, we will have a clear picture of the quenching mechanisms for these phosphors in LED packages. This will greatly aid the LED package design to optimize the phosphor conversion efficiency for UV-LED based systems. For example, if it is clear that strong thermal quenching is occurring in the LED package, then new packages will be designed and tested where the phosphor layer does not experience high temperatures. This could involve moving the phosphor layer away from the LED chip or different thermal management schemes for the phosphor layer. Other modifications of the phosphor coatings in the LED package will also be considered depending upon the phosphor performance and spectroscopy.

This Task will be completed at the end of the funding period, with the anticipated outcome of high efficacy white light LED devices.

TASK 6

Program Management

Important for the successful completion of the first year of our project was the close collaboration of the UGA and GE teams. Weekly phone conferences were held to discuss the current and upcoming tasks, in addition to hundreds of e-mails and additional phone calls. The collaboration was flawless, as an example, samples requested by UGA were synthesized and delivered in less than a week.
We like to note the educational aspect of the project, two students graduated during the first twelve month, and a third (P. Schmidt) is scheduled to graduate at the end of the funding period.

PRESENTATIONS

4^{th} International Conference on Solid State Lighting, SPIE Meeting, Denver, Colorado 2004

Development of New Phosphors for LED Based Illumination

A.A. Setlur, G. Chandran, D. Hancu, A.M. Srivastava, and E. Radkov

206^{th} Meeting of The Electrochemical Society, Honolulu, Hawaii, October 3-8, 2004

Photoionization and Quenching in $SrSiO_4$:Eu^{2+}

H.A. Comanzo, A.A. Setlur, A.M. Srivastava, P. Schmnidt, B. Wen, and U. Happek

Photoionization of Eu^{2+} Ions in $Sr(SCN)_2$

C.Wickleder, B.Wen, and U. Happek

$Eu^{2+} \rightarrow Mn2+$ Energy Transfer in the UV-LED Phosphor $Ca_5(PO_4)_3Cl$

H.A.Comanzo, A.A. Setlur, A.M. Srivastava, P. Schmidt, B. Wen, and U. Happek

Thermoluminescene Excitation Measurements of Photoionization in Doped Insulators

Jay Fleniken, PhD Thesis, The University of Georgia (2004).

Thermally Stimulated Luminescence Excitation Spectroscopy as a Technique to Measure the Ionization Energy of $Sr(SCN)_2$:Eu^{2+}

B. Wen, Master's Thesis, The University of Georgia (2004).